A STUDY OF THE STEREOELECTRONIC FACTORS INFLUENCING NUCLEOPHILIC ATTACK AT PHOSPHORUS

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A STUDY OF THE STEREOELECTRONIC FACTORS

INFLUENCING NUCLEOPHILIC ATTACK AT PHOSPHORUS

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

CHAPTER I

INTRODUCTION

Although the mechanisms for nucleophilic attack at carbon are fairly well understood, the details of similar processes involving attack on second-row elements are far less clear. The difficulty in obtaining unequivocal evidence for the geometries of intermediates and transition states is inherent in the ability of the second-row elements to expand their valence shells and thus utilize various d-orbitals in forming hybrid orbitals with a variety of geometries depending upon the d-orbitals involved.

d-Orbital Hybridization

Hybridization of the d_{z^2}-orbital with a p_z-orbital of the same principal quantum number leads to two equivalent pd hybrid orbitals directed along the z axis. Combination of these with the three sp^2 hybrid orbitals can give rise to a trigonal bipyramid structure with the sp^2 orbitals defining the equatorial plane (Figure 1). Hybridization of the $d_{x^2-y^2}$ with the p_x-, and s-orbitals leads to a square planar structure (Figure 2). Still a third geometry results from the hybridization of one of four equivalent sp^3 hybrid orbitals with the d_{xy}-orbital to give a structure of the geometry shown in Figure 3 in which there is a 71° angle between the axes of the two spd hybrid orbitals[1].

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1. R. J. Gillespie, J. Chem. Soc., 1002 (1953).

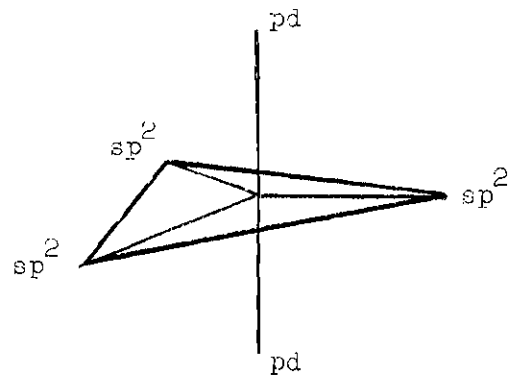


Figure 1. Geometry Resulting from Combination of Three sp^2 Hybrid Orbitals with Two pd Hybrid Orbitals

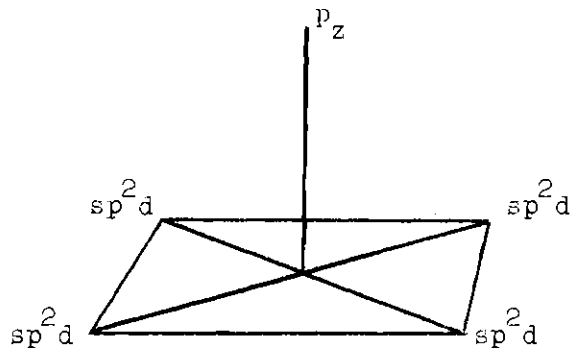


Figure 2. Geometry Resulting from Combination of Four sp^2d Hybrid Orbitals with the p_z Orbital

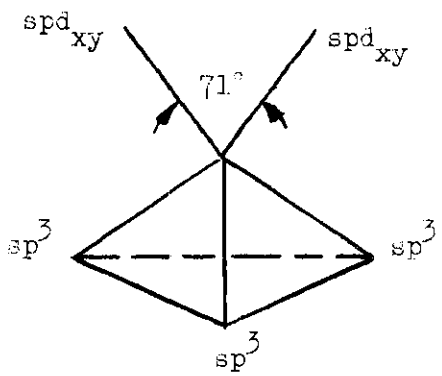
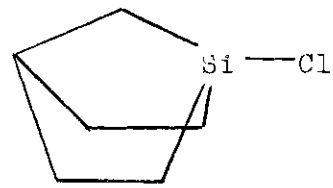


Figure 3. Geometry Resulting from Combination of Two spd Hybrid Orbitals with Three sp^3 Hybrid Orbitals

Electron diffraction studies of PCl_5, PF_5, PCl_3F_2 and PBr_5 have established the trigonal bipyramid structure for these molecules in the vapor phase[2]. Wheatley and Wittig[3] have established the square pyramid structure for $Sb(C_6H_5)_5$ in the solid state with the antimony atom located about 0.5 Å above the basal plane. No stable compounds with a second-row element in a sp^3-spd hybridized state have been reported, but this geometry is appealing when one considers the rapid rate of hydrolysis of strained bicyclosilicon halides such as 1-chloro-1-silabicyclo[2,2,1]-heptane, (1)[4]. In contrast, the analogous alkyl chloride is extremely unreactive towards nucleophilic reagents[5,6].



1

With each of these geometries there is more than one possible set of orientations for the entering and leaving groups. In the case of

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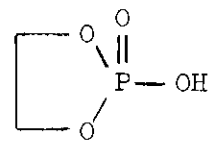
2. L. O. Brockway and J. Y. Butler, J. Am. Chem. Soc., 60, 1836 (1930).
3. P. J. Wheatley and G. Wittig, Proc. Chem. Soc., 251 (1962).
4. L. H. Sommer and O. F. Bennett, J. Am. Chem. Soc., 79, 1008 (1957).
5. P. D. Bartlett and L. H. Knox, J. Am. Chem. Soc., 61, 3184 (1939).
6. P. D. Bartlett and E. S. Lewis, J. Am. Chem. Soc., 72, 1005 (1950).

phosphate esters, the various possibilities were limited somewhat by the elegant work of Haake and Westheimer[7] in their study of the acid-catalyzed O^{18} exchange of ethylene phosphoric acid (2). It had previously



2

been noted that the salts of ethylene phosphate hydrolyze in base about 10^7 times as fast as those of dimethyl phosphate[8] and that the same rate enhancement exists for the hydrolysis of the cyclic hydrogen phosphate in acid[9,10]. Haake and Westheimer found that the rate of O^{18} exchange was similarly enhanced by the presence of the five-membered ring. Reasoning that such a pronounced increase in the rates of both hydrolysis and O^{18} exchange indicated a common mechanism for the two processes, these workers were able to eliminate one of the possible orientations of entering and leaving groups in the trigonal bipyramid structure, and to predict the stereochemical consequences for the reaction proceeding through structures having the geometry of the trigonal bipyramid or

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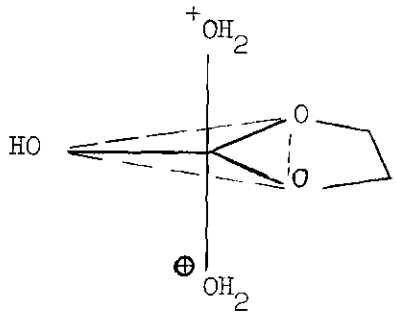
7. P. C. Haake and F. H. Westheimer, J. Am. Chem. Soc., 83, 1102 (1961).
8. [illegible]. Kumamoto, J. R. Cox, Jr., and F. H. Westheimer, J. Am. Chem. Soc., 78, 4858 (1956).
9. F. H. Westheimer, Chem. Soc. (London) Spec. Publ., 8, 1 (1957).
10. J. R. Cox, Jr., Ph.D. Thesis, Harvard Univ. (1959).

square pyramid. The intermediates considered are shown in Figure 4. Since the kinetic equation has the form

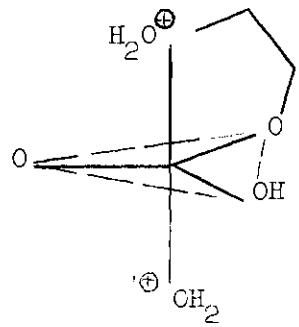
$$\text{rate} = k_2(\text{phosphate})(H^{\oplus})$$

each must contain a molecule of phosphate and water, and a proton, corresponding to nucleophilic attack by water on the conjugate acid of the substrate. The left-hand member of each pair represents the transition state or intermediate for exchange, that on the right, the transition state or intermediate for hydrolysis. In the transition states postulated for nucleophilic attack on phosphorus (3-a and 3-b) the entering and leaving groups both occupy the axial positions of the trigonal bipyramid. The O-P-O bond angles of the rings differ for the two processes; in 3-a it is 120°, in 3-b, 90°. If strain in the five-membered ring of the reactant is the source of the enhanced rates of both acid-catalyzed hydrolysis and O^{18} exchange, it would seem that the change in the O-P-O bond angle should be the same for both processes. The remaining possibility for the trigonal bipyramid is represented by 4-a and 4-b. In both of these structures, the O-P-O bond angle, which is part of the ring, is about 90° and the entering and leaving groups occupy equatorial positions. That this case results in inversion of configuration can be seen from Figure 5, where X is the entering group and C is the leaving group.

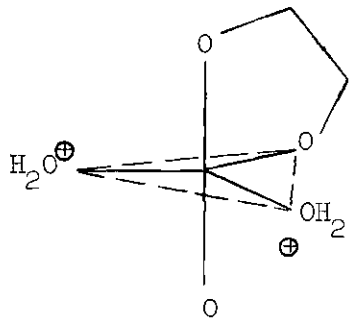
Formulas 5 and 6 represent the two possibilities for the orientation of entering and leaving groups for the square pyramid. In all four cases, the entering and leaving groups are in the basal plane. In formulas 5-a and 5-b, however, the entering and leaving groups are adjacent to each other and retention of configuration results, while in 6-a and 6-b the



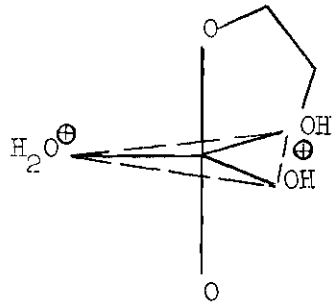
3-a



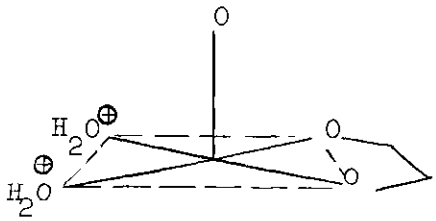
3-b



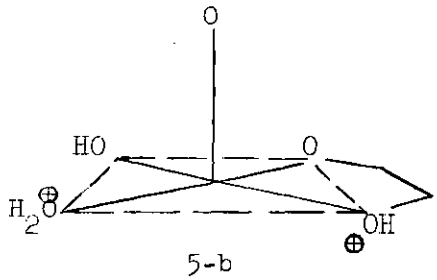
4-a



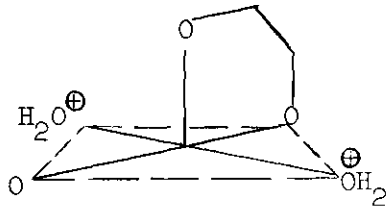
4-b



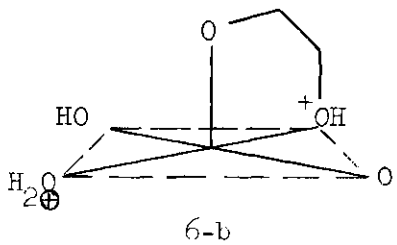
5-a



5-b



6-a



6-b

Figure 4. Possible Intermediates or Transition States for the Acid-Catalyzed Hydrolysis of Ethylene Phosphoric Acid

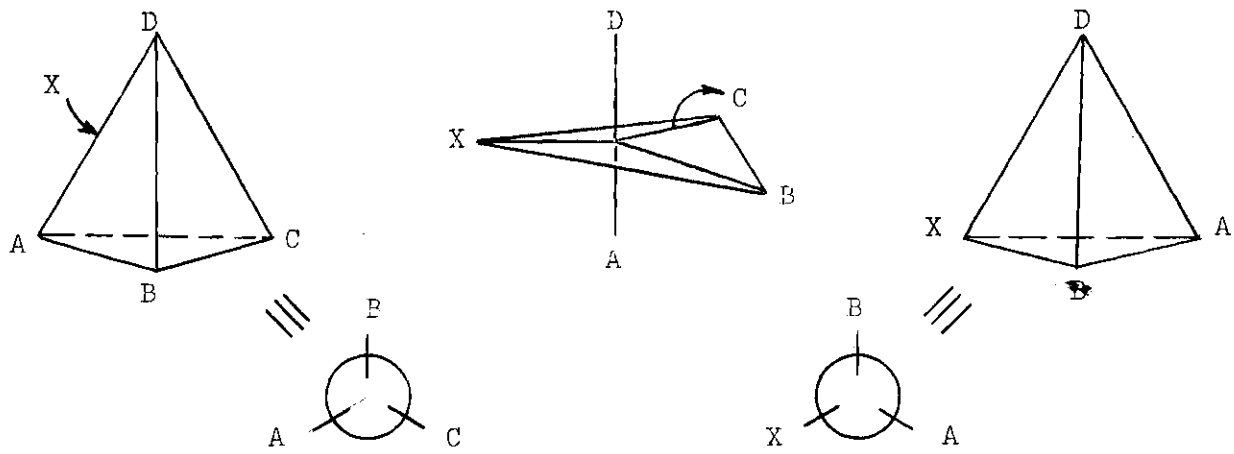


Figure 5. Demonstration that Inversion of Configuration Accompanies Nucleophilic Substitution at Phosphorous via 4

entering and leaving groups are opposed, and inversion of configuration occurs as shown in Figure 6.

Basic Decomposition of Tetraalkyl Phosphonium Salts

Treatment of tetraalkyl phosphonium salts with base or the pyrolysis of the hydroxides results in the formation of a tertiary phosphine oxide and an alkane[11]. The products of this reaction differ from those

$$R_4P^{\oplus}OH^{\ominus} \rightarrow R_3P{=}O + RH$$

obtained from the pyrolysis of the analogous ammonium hydroxides, the latter affording an olefin and a tertiary amine. An olefin and tertiary phosphine can be obtained from the pyrolysis of the phosphonium hydroxide only if the abstraction of a proton from the β-carbon of one of the alkyl

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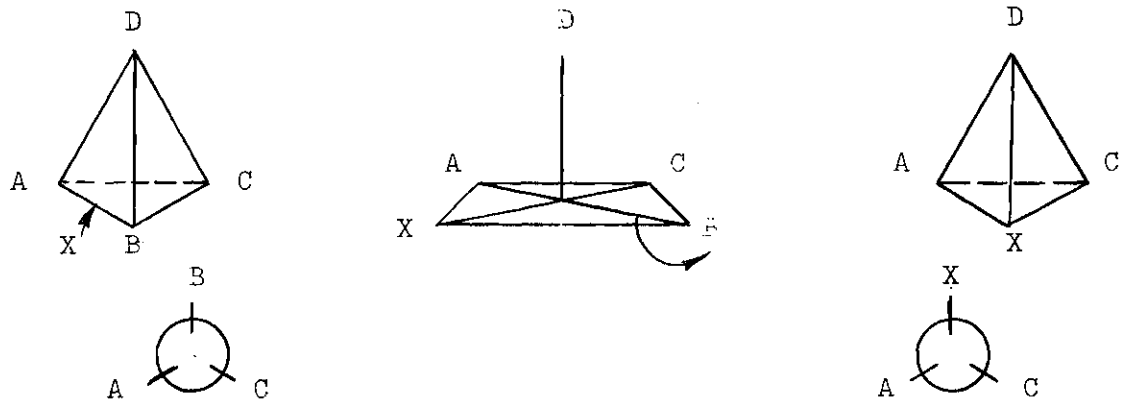
11. A. Cahours and A. W. Hofmann, Ann., 104, 1 (1875).

Entering and leaving groups adjacent; retention



Entering and leaving groups opposed; inversion

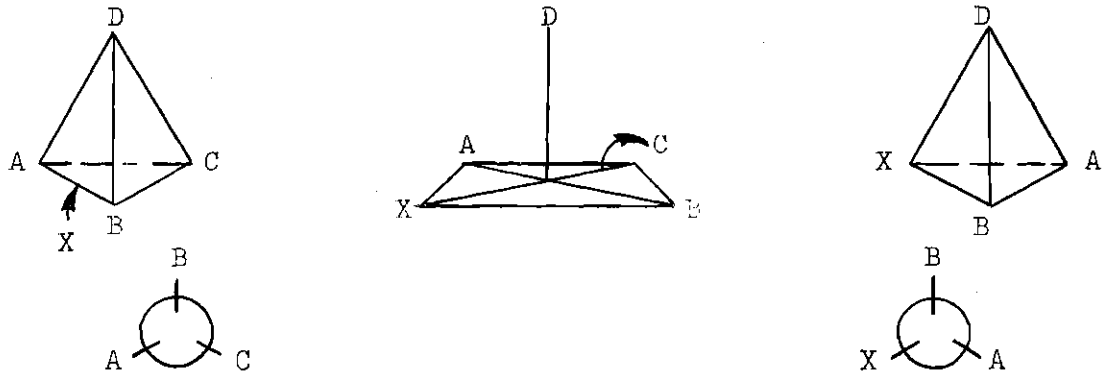


Figure 6. Demonstration of the Stereochemical Consequences of Nucleophilic Substitution at Phosphorus via 5 and 6

groups results in the formation of a highly stabilized carbanion. Thus the pyrolysis of (2,2-diphenylethyl)tributylphosphonium hydroxide gives 90% diphenylethylene and 10% diphenylethane, (Eq. 2) while (2-phenylethyl)tributylphosphonium hydroxide gives only 5% styrene, 88% ethylbenzene and 7% butane (Eq. 3).

$$(n\text{-}Bu)_3\overset{\oplus}{P}\text{-}CH_2\text{-}CH(C_6H_5)_2 \rightarrow \underset{90\%}{(n\text{-}Bu)_3P + CH_2 = C(C_6H_5)_2} \quad \text{(Eq. 2)}$$

$$+ \underset{10\%}{(n\text{-}Bu)_3P = O + CH_3\text{-}CH(C_6H_5)_2}$$

$$(n\text{-}Bu)_3\overset{\oplus}{P}\text{-}CH_2\text{-}CH_2(C_6H_5) \rightarrow \underset{5\%}{Bu_3P + C_6H_5\text{-}CH = CH_2} \quad \text{(Eq. 3)}$$

$$+ \underset{88\%}{(nBu)_3P = O + C_6H_5\text{-}CH_2CH_3}$$

$$+ (n\text{-}Bu)_2\ddot{P} - CH_2\text{-}CH_2(C_6H_5) + \underset{7\%}{CH_3CH_2CH_2CH_3}$$

The mechanism proposed by Fenton and Ingold[12] for the formation of alkane and tert-phosphine oxide involves nucleophilic attack by hydroxide ion to form a pentacovalent phosphorus intermediate (Eq. 4). This intermediate, upon abstraction of a proton by another hydroxide ion, loses a carbanion to form a tert-phosphine oxide.

$$R_4P^{\oplus}OH^- \rightleftarrows R_4P\text{-}OH \overset{OH^{\ominus}}{\underset{H_2O}{\rightleftarrows}} R_3P^{\ominus}O \rightleftarrows R_3\overset{\oplus}{P}\text{-}\overset{\ominus}{O} + R^{\ominus} \quad \text{(Eq. 4)}$$

$$R^{\ominus} + H_2O \rightarrow RH + HO^{\ominus}$$

Confirmatory evidence for this mechanism was obtained by a study of the

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12. G. W. Fenton and C. K. Ingold, J. Chem. Soc., 2342 (1929).

kinetics of the alkaline decomposition of a series of tetrabenzylphosphonium iodides by Zanger, VanderWerf and McEwen, and a series of benzyltriphenylphosphonium halides by Hoffman[13,14]. Both papers reported that the reaction was first-order in phosphonium salt and second-order in hydroxide ion, although Hoffman found that the third-order rate constant was strongly dependent upon the initial concentration of the phosphonium salt. A plot of the log of the third-order rate constants for salts of the type m- or p-X-$(C_6H_4CH_2)P(C_6H_5)_3Br$ versus the Hammett substituent constant for the substituent X yielded a straight line with a ρ=4.7. These data confirm the Fenton-Ingold mechanism if the additional requirement is made that the rate-determining step be the expulsion of the alkyl group to form a carbanion.

The Stereochemistry of the Alkaline Decomposition of Quaternary Phosphonium Salts

VanderWerf and co-workers succeeded in resolving racemic methylethylphenylbenzylphosphonium iodide by fractional crystallization of the salts resulting from metathesis with optically active silver dibenzoyl hydrogen tartrate[15]. Reaction of the optically pure phosphonium salt with the base gave methylethylphenylphosphine oxide whose optical rotation was opposite that of the phosphonium salt. The relative configurations of the reactant and product could be established in two ways. Reaction of

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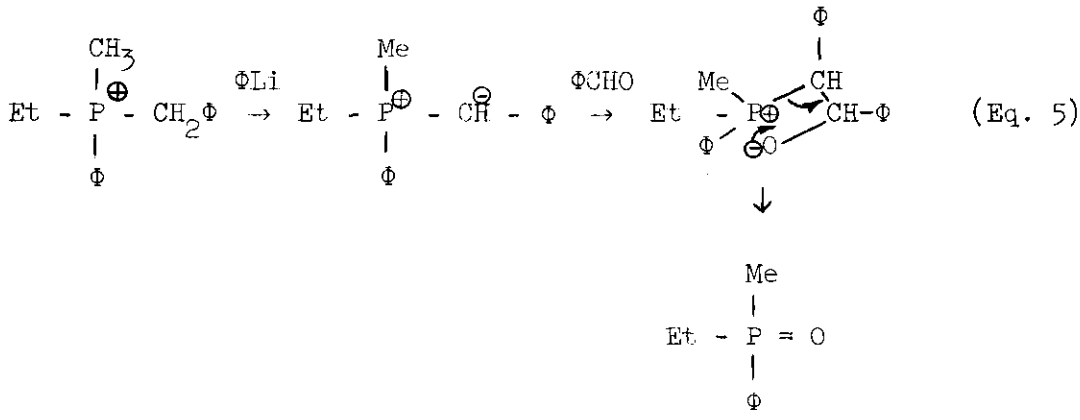
13. M. Zanger, C. A. VanderWerf and W. E. McEwen, J. Am. Chem. Soc., 81, 3806 (1959).

14. H. Hoffman, Ann., 634, 1 (1960).

15. K. F. Kumli, C. A. VanderWerf and W. E. McEwen, J. Am. Chem. Soc., 81, 248 (1959).

benzaldehyde with methylethylphenylbenzylidenephosphorane prepared from the optically active phosphonium salt gave a 70% yield of methylethylphenylphosphine oxide, the optical rotation of which was of the same magnitude as that obtained from the basic decomposition of the phosphonium salt, but of the opposite sign. Hence, though both methods of obtaining the phosphine oxide appear to be both stereospecific and product specific, one process leads to inversion of configuration and the other to retention[16]. Schöllkopf[17] has proposed that the Wittig reaction proceeds through a four-membered cyclic transition state, and thus results in retention of configuration about phosphorus (Eq. 5).



(Eq. 5)

Horner, et al.[18] have prepared optically active methylethylphenylphosphine by electrolytic reduction of the optically active benzyl iodide salt. Requaternization with benzyl iodide gives the original salt with overall

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16. A. Bladé-Font, C. A. VanderWerf and W. E. McEwen, J. Am. Chem. Soc., 82, 2396 (1960).

17. U. Schöllkopf, Angew. Chem., 71, 260 (1959).

18. L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffmann and P. Peck, Tetrahedron Letters, 161 (1961).

retention of configuration, while treatment of the optically active phosphine with hydrogen peroxide yields ethylmethylphenylphosphine oxide whose optical rotation is of the same sign as the phosphine. If one assumes that both the quaternization and oxidation of the phosphine do not involve displacements on phosphorus, and thus proceed with retention of configuration, one again arrives at the conclusion that the basic decomposition of the phosphonium salt occurs with inversion of configuration about phosphorus, as shown in Figure 7.

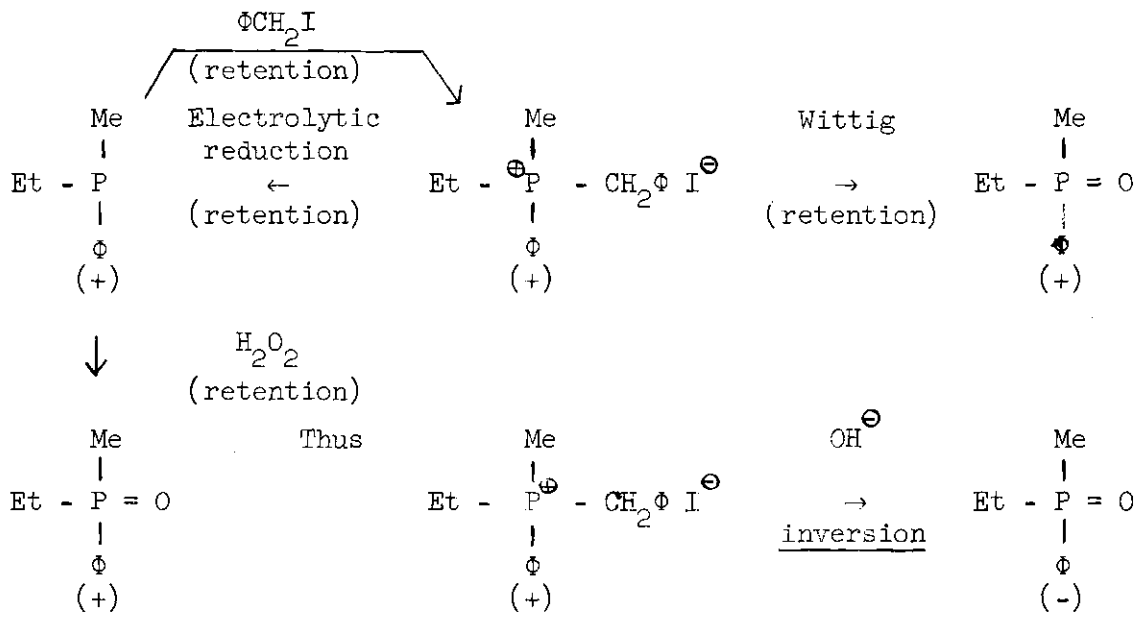


Figure 7. Transformations of Optically Active Phosphines and Phosphonium Salts

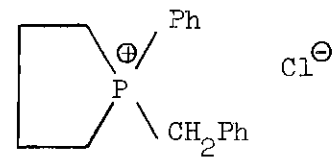
Two of the previously mentioned intermediates will lead to inversion of configuration about phosphorus: the trigonal bipyramid with the entering and leaving groups both occupying equatorial positions, and the square pyramid structure in which the entering and leaving groups lie opposite each other in the basal plane. On the basis of present experimental

evidence it is impossible to distinguish between the two.

Reactivity Effects of Five-Membered Rings Attached to Phosphorus

It is not presently known whether the high susceptibility to nucleophilic attack of cyclic phosphates containing five-membered rings depends on the composition of the ring, or whether the ring size alone determines the reactivity of cyclic phosphates. The currently accepted[19] explanation for rapid hydrolysis of ethylene hydrogen phosphate involves the postulate of "back-bonding," or dative d-π bonding, in which delocalization of unshared electron pairs on the ester oxygen atom by unoccupied d-orbitals on electropositive phosphorus results in stabilization of the phosphate. It is hypothesized that the stereo-electronic requirements for the delocalization are such that the five-membered ring inhibits d-π bonding and destabilizes the cyclic phosphate relative to its acylic analog, even though the transition states for the slow steps of the hydrolyses are of approximately the same energy in the two compounds.

The work to be described deals with the kinetics of the alkaline decomposition of cyclotetramethylenephenylbenzylphosphonium chloride (3). The objectives of this investigation are two-fold:



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19. E. T. Kaiser, M. Panar, F. H. Westheimer, J. Am. Chem. Soc., 85, 602 (1963)

1. To determine if the basic decomposition of a phosphonium salt containing a five-membered ring without oxygen is subject to the same increase in rate as the cyclic phosphate compared to its acyclic analog.

2. To determine whether or not the five-membered ring changes the kinetic form of the reaction.

It will be noted that the first objective has a direct bearing on the validity of Westheimer's "back-bonding" theory. The second objective is intriguing when one considers the possibility that the ring might stabilize the pentacovalent intermediate to such an extent relative to the reactants that the reaction becomes first order with respect to hydroxide. This would require that the first step, nucleophilic attack by hydroxide, be rapid and essentially irreversible. Hence, the reactant would be a relatively stable covalent phosphonium hydroxide.

CHAPTER II

EXPERIMENTAL

Instrumentation

A modified Hershberg melting point apparatus equipped with an electric stirrer and Anschütz thermometers was used for all melting points. The NMR Spectra were obtained using the Varian Associates Model A-60 Nuclear Magnetic Resonance Spectrometer.

Synthetic

Phenylphosphonous dichloride:

Phenylphosphonous dichloride was synthesized by a modification of the method of Buchner and Lockhard[20].

Phosphorus trichloride, 330 g. (2.40 mole), benzene, 46.8 g. (0.80 mole), and anhydrous aluminum chloride, 106 g. (0.80 mole), were boiled under reflux on a steam bath for four hours in a one-liter, three-necked flask equipped with a Friedrichs condenser and a mechanical stirrer. The hydrogen chloride evolved in the course of the reaction was led to the rear of an efficient hood through a length of Tygon tubing attached to the condenser outlet. The steam bath was removed and 112.6 grams (0.80 moles) of phosphorus oxychloride was added by means of a dropping funnel while vigorous stirring was maintained. Two hundred milliliters of petroleum ether was added and the solid aluminum chloride-phosphorus oxychloride complex allowed to settle. The ether extract was

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20. B. Buchner and L. B. Lockhard, J. Am. Chem. Soc., 73, 255 (1951).

decanted from the solid and the latter was washed with eight 200 ml. portions of ether. The original extract and ether washings were combined and the low boiling liquids removed by distillation on a steam bath at atmospheric pressure. The residual yellow oil was fractionated through a 30 cm., vacuum-jacketed column packed with glass helices to yield 84 grams of phenylphosphonous dichloride, b. p. 99-100° at 15 mm. Hg. Yield, 82%, based on benzene.

Cyclotetramethylenephenylphosphine:

The method of preparation of cyclotetramethylenephenylphosphine is a modification of that of Grüttner and Krause[21]. The reactions were carried out in a one-liter, three-necked flask fitted with a Friedrichs condenser, mechanical stirrer and dropping funnel. All operations up to the isolation procedure were done in an atmosphere of dry nitrogen. Diethyl ether used in the preparation of the Grignard reagent was dried by distilling from an ethereal solution of lithium aluminum hydride. The Grignard reagent, prepared from 29 grams (1.2 moles) of magnesium turnings and 108 grams (0.50 moles) of 1,4-dibromobutane in 500 ml. of diethyl ether, was cooled to 0-5° with an ice bath and a solution of 71 grams (0.40 moles) of phenylphosphonous dichloride in 200 ml. of dry ether was added dropwise over a period of two hours. The reaction mixture was boiled under reflux for about thirty minutes, cooled in an ice bath and transfered to a three-liter Erlenmeyer flask. One liter of water was added, slowly at first, to destroy the excess Grignard. This was followed by sufficient conc. ammonium hydroxide and solid ammonium

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21. G. Grüttner and E. Krause, Ber., 49, 437 (1916).

chloride to buffer the solution at pH 9 - 10. A similarly buffered solution of 400 grams of tetrasodium ethylenediaminetetraacetate in one liter of water was slowly added to the reaction mixture with stirring. The resulting aqueous solution was then extracted with five 500 ml. portions of diethyl ether. The volume of the combined ether extracts was reduced to 500 ml. under reduced pressure. The resulting ether solution was dried over anhydrous sodium sulfate and filtered. The remaining ether was stripped under vacuum, yielding a thick syrup. Distillation at reduced pressure gave cyclotetramethylenephenylphosphine as the only material which distilled under 200°, b. p. 85-90° at 0.1 mm. Yield, 19 grams (31%).

Benzylcyclotetramethylenephenylphosphonium chloride:

Ten grams of cyclotetramethylenephenylphosphine was treated with 20 grams of benzyl chloride. The flask became quite warm and after about five minutes, a large mass of white crystals formed. After standing overnight the crude phosphonium salt was washed several times with ether and dried under high vacuum. Recrystallization three times from hot 1,2-dimethoxyethane-abs. ethanol and drying overnight under vacuum gave fine white crystals, m. p. 172-173°. Chloride analysis by potentiometric titration with Ag^+: cal'd for $C_{17}H_{20}PCl$, 12.3%; found 12.4%.

Kinetics

The kinetics of the basic decomposition of benzylphenylcyclotetramethylenephosphonium chloride were studied in the following manner: an aqueous solution 1.00 M in potassium chloride and ca. 0.10 M in sodium hydroxide was brought to the proper temperature in a constant-temperature

bath, and 50.0 ml. of the solution was pipetted into a 100 ml. polyethylene bottle containing about 725 mg. of the phosphonium salt so that the initial concentration of the latter was about 0.05 M. The change in concentration of hydroxide ion with time was determined by withdrawing 4.00 ml. aliquotes and quenching with 5.00 ml. of 0.1 M hydrochloric acid. The excess acid was back-titrated to the phenolphthalein end-point with 0.05 M sodium hydroxide. Bath temperatures were constant to within ± 0.05° on the basis of a N.B.S. calibrated thermometer. The time lag between the mixing of the solutions and removal of the first aliquot for the point taken as zero time was never more than 30 seconds.

CHAPTER III

RESULTS

The integrated rate equation for a reaction of the stoichiometry

$$A + B \rightarrow \text{products}$$

and following a third-order rate law of the type

$$\text{rate} = k_3(A)^2(B)$$

is given by Equation 6[22]

$$\frac{1}{B_0-A_0}\left(\frac{1}{A}-\frac{1}{A_0}\right)+\frac{1}{(B_0-A_0)^2}\ln\frac{B_0A}{A_0B}=k_3t \qquad \text{(Eq. 6)}$$

where A_0 and B_0 are the initial concentrations of the reactants, A and B the concentrations at time, t, and k_3 is the third-order rate constant. For a third-order reaction of the required stoichiometry, a plot of the left-hand side of Eq. 6 versus t will yield a straight line with a slope equal to k_3. Such a plot for the runs at 60° and 70° did indeed yield straight lines confirming the third-order kinetics observed in the previously mentioned studies of noncyclic phosphonium salts (Figure 8). Only initial rates were obtained from runs at 50.0° and 80.0°, but these were in accord with the rate constants obtained from the runs at 60°

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22. A. A. Frost and R. G. Pearson, Kinetics and Mechanism, 2nd ed., New York: John Wiley and Sons, Inc., 1960, p. 21.

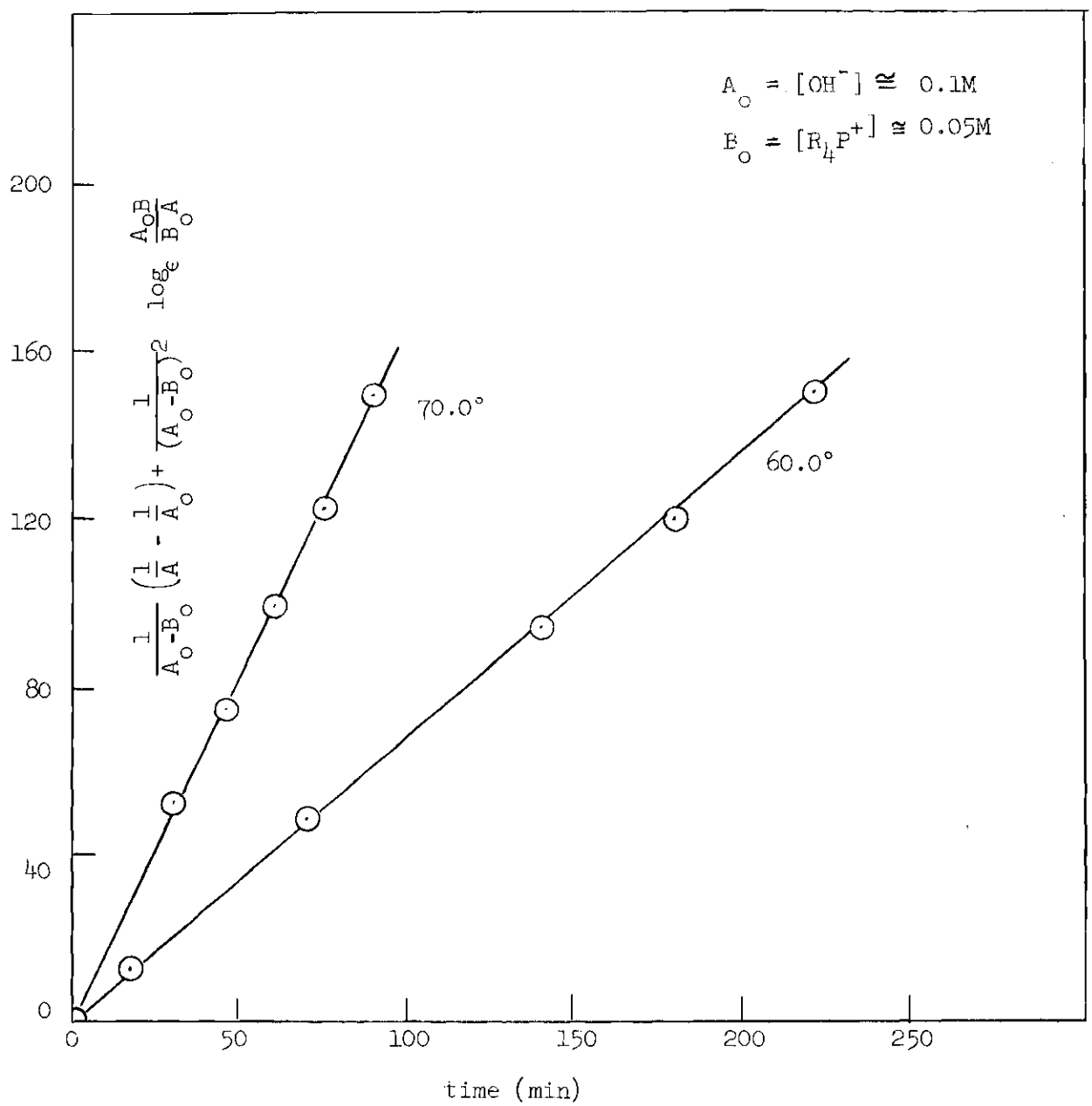

Figure 8. Third-Order Test Plots for the Basic Decomposition of Phenylbenzylcyclotetramethylene Phosphonium Chloride

and 70° (Figure 8) as judged from the Arrhenius plot (Figure 9).

The rate constants obtained at the various temperatures, along with an extrapolation of the data to 99.4°, are contained in Table 1.

Table 1. Summary of Rate Data for the Basic Decomposition of Phenylbenzylcyclotetramethylene Phosphonium Chloride. $[OH^{\oplus}]_0 \cong 0.1M$, $(R_4P^{\oplus})_0 \cong 0.05M$

t (°C)	k_3 ($M^{-2}min^{-1}$)
50.0°	0.189
60.0°	0.673
70.0°	1.65
80.0°	4.60
99.4°	26.6 *

*Extrapolated from lower temperature. See Figure 9.

The energy of activation calculated from the slope of the Arrhenius plot was 23.4 kcal/mole.

The initial concentrations of reactants and potassium chloride used in these studies were identical to those used by Zanger, VanderWerf and McEwen in their investigation of the kinetics of the basic decomposition of methylethylphenylbenzylphosphonium iodide. The average specific rate constant obtained at 99.4° was $k_3 = 7.90\ M^{-2}hr.^{-1}$. Extrapolation of the data for the cyclic phosphonium salt to 99.4° led to a specific third-order rate constant $k_3 = 26.6M^{-2}min.^{-1}$. The relative rates of the cyclic and acyclic phosphonium salts are shown in Figure 10.

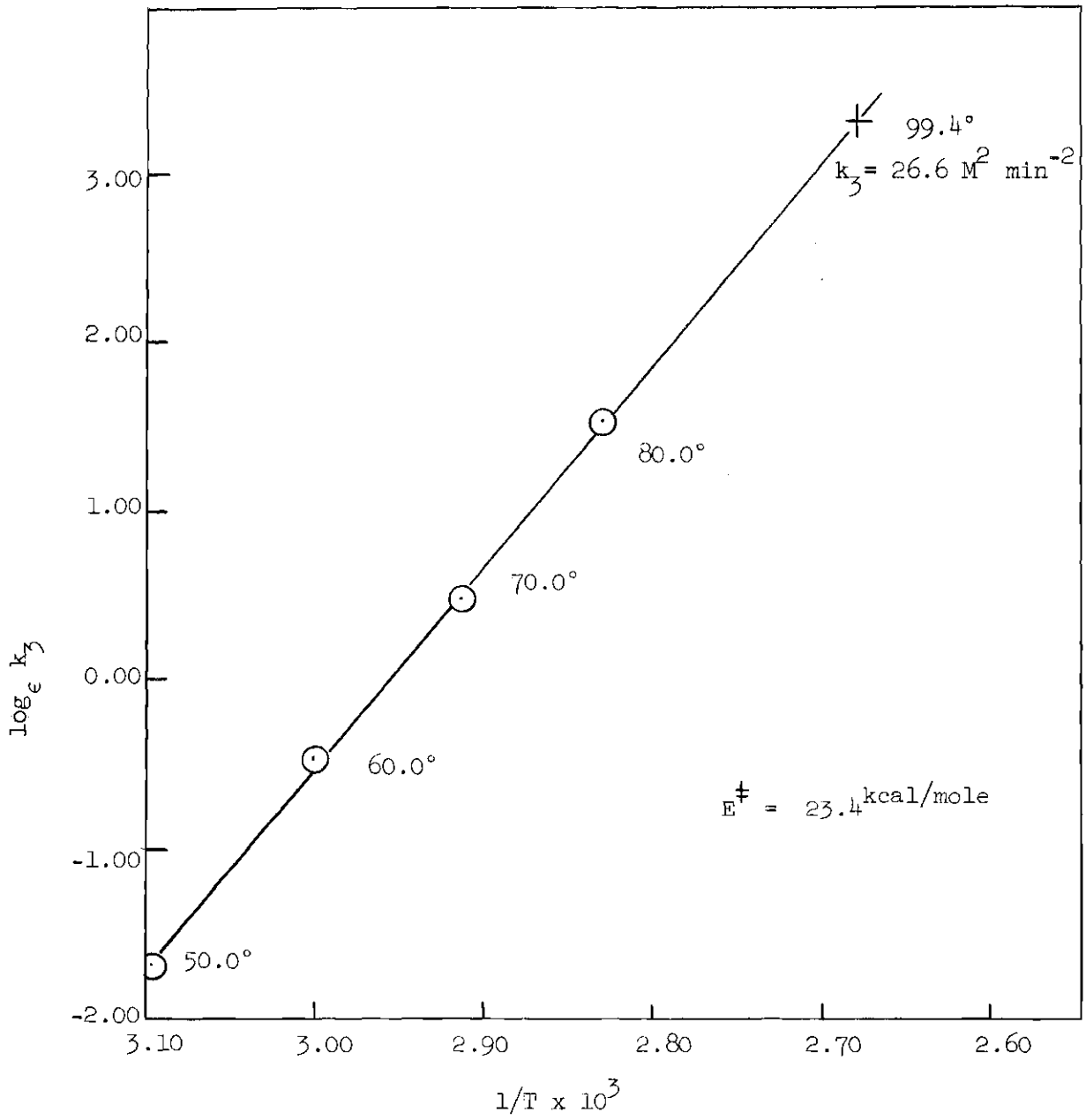

Figure 9. Arrhenius Plot for the Basic Decomposition of Phenylbenzylcyclotetramethylene Phosphonium Chloride

1 200

Figure 10. Relative Rates for the Basic Decomposition at 99.4°

CHAPTER IV

DISCUSSION

The experimental results can be summarized as follows:

1. The basic decomposition of the cyclic phosphonium salt shows good third-order kinetics.

2. The inclusion of the five-membered ring increases the rate of basic decomposition by a factor of 200 over that of its acyclic analog.

The third-order kinetics indicates that the mechanism of the reaction is the same as that for non-cyclic phosphonium salts.

In attempting to rationalize the relative rates of the basic decomposition of the cyclic and noncyclic phosphonium salts one should note that the accelerating effect of the five-membered ring is smaller by a factor of about 50,000 than in the analogous phosphates. This in itself is in agreement with the postulated effect of partial d-π bonding in imparting extra stability to the noncyclic phosphates. In applying this argument, it was assumed that the energy of the transition states for the hydrolysis of dimethyl and ethylene phosphate were the same, and that the sole kinetic effect of the five-membered ring in ethylene phosphate is to sterically inhibit d-π bonding in the unreacted ethylene phosphate molecule, and thus decrease the activation energy for the hydrolysis of the cyclic ester relative to dimethyl phosphate.

The 200-fold increase in the rate of basic decomposition of the

cyclic phosphonium salt relative to the noncyclic salt can be rationalized in more conventional terms. Nucleophilic attack by hydroxide ion on phosphorus to form a pentacovalent intermediate possessing the geometry of either a trigonal bipyramid or a square pyramid should result in a contraction of the C-P-C bond from the normal tetrahedral angle of about 109° to 90° with a resultant expansion of the C-C-P bond angle if the ring remains planar. By folding the ring (Figure 11) an envelope conformation is obtained whereby all C-C-P bond angle strain is relieved. The important factor, though, is the removal of four eclipsed hydrogen interations. Kemp and Pitzer[23] noted that the poor agreement between the

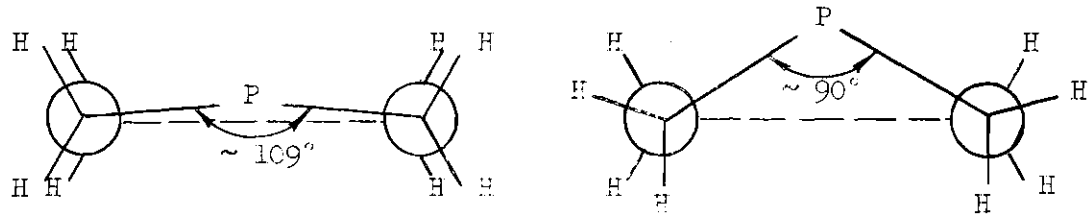

Figure 11. Removal of Four Eclipsed H-H Interactions by Contraction of the C-P-C Bond Angle from ~ 109° to 90° with Simultaneous "Folding" of the Five-Membered Ring

experimental values for the entropy and enthalpy of ethane and those calculated from statistical mechanics could be alleviated by assuming a potential barrier of about 3 kcal/mole for free rotation about the carbon-carbon single bond, yielding a value of about 1 kcal/mole for each

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23. J. D. Kemp and K. S. Pitzer, J. Chem. Phy., 7, 749 (1936).

eclipsed hydrogen-hydrogen interaction. If in this case, as with ethylene and dimethyl phosphate, it is assumed that the transition states for the rate-determining step are of the same energy, one can tentatively conclude that the cyclic phosphonium salt is less stable than its non-cyclic analog by about 4 kcal/mole. No data are presently available for the frequency factors or the energies of activation for the basic composition of noncyclic phosphonium salts. However, if one makes the rather naive assumption that the ratio of frequency factors for the cyclic and noncyclic salts is 5/6 (corresponding to the steric blocking of nucleophilic attack at one of the six edges of the tetrahedron by the five-membered ring), the difference in the activation energies can be calculated knowing the relative rates at 99.4° by means of Equation 7:

$$\ln \frac{k_{cyc}}{k_{non}} = \frac{A_{cyc}}{A_{non}} \; e^{\frac{-(E_{cyc}-E_{non})}{RT}} \qquad \text{(Eq. 7)}$$

With $\frac{k_{cyc}}{k_{non}} = 200$ and assuming $\frac{A_{cyc}}{A_{non}} = \frac{5}{6}$.

$$(E_{cyc}-E_{non}) = -4.1 \frac{\text{kcal}}{\text{mole}}$$

It is not surprising that the cyclic phosphonium salt should be less stable than its acyclic analog when one considers that cyclopentane itself is less stable than pentane by about 6 kcal/mole[24].

A similar calculation for the phosphates involving the same

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24. J. Coops, H. Van Kamp, W. H. Lambregets, J. Visser and H. Dekker, Rec. Trav. Chim., 79, 1226 (1960).

assumption for the ratio of the frequency factors gives a difference in activation energies for dimethyl and ethylene phosphate of 9 kcal/mole. Thermochemical measurements of the heats of saponification of these esters show the cyclic ester to be 5 kcal/mole less stable than the dimethyl phosphate, if the products of saponification of the two esters are taken as the point of zero energy in each case[25]. The 4 kcal/mole difference between the difference in activation energies for the cyclic and noncyclic compounds calculated by means of Equation 7 and the difference in stabilities of the unreacted species as shown by means of the heats of saponification must indicate that one or both of the following assumptions is invalid:

1. that the frequency factors for the hydrolysis of dimethyl and ethylene phosphate are the same or at least comparable,

2. that the energy of the transition states for the rate determining step are the same.

Assuming the first assumption to be false and that the total difference in the energies of activation for the hydrolysis of the two esters is the 5 kcal/mole difference in stabilities of the unreacted species, it can be calculated from Equation 7 that the ratio of the frequency factors is about 3,000. This corresponds to a difference in entropies of activation of about 16 e.u. This would appear to be a rather large difference to attribute to steric factors alone, and the question of whether the pronounced difference in the rates of hydrolysis of the

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25. E. T. Kaiser, M. Panar and F. H. Westheimer, J. Am. Chem. Soc., 85, 602 (1963).

cyclic and noncyclic phosphates can be attributed to anomalous differences in the entropies of activation, or the stabilizing influence of the five-membered ring on the pentacovalent intermediate indicates the necessity for obtaining accurate values for the activation parameters for the hydrolysis of these compounds.